[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

The Mechanism of the Base-catalyzed Rearrangement of Organopolysiloxanes[1]

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The mechanism of the polymerization of polydimethylsiloxanes with strong bases is discussed. This mechanism involves two distinct although related steps: (a) the entry of the catalyst molecule into the siloxane system, and (b) the continued action of the catalyst molecule, or some part of it, in the reshuffling of siloxane linkages. It is shown that a rate-controlling factor in the polymerization of octamethylcyclotetrasiloxane is the base strength of the catalyst. A study of the base-catalyzed polymerization of dimethylsiloxanes at room temperature in homogeneous alcoholic systems also is discussed; the base-strength effect is clearly demonstrated. The nature of the silicon–oxygen–alkali metal bond has been investigated by measurements of conductivity in siloxane and alcoholic media, both at room and elevated temperatures.

I. Introduction

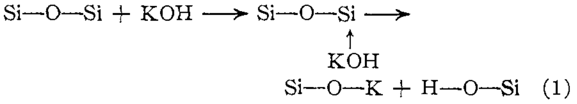
There are two general methods that are used for the rearrangement or polymerization of polyorganosiloxanes: catalysis with acids,[2-5] or with strong bases.[6] The acid catalysis has been used for the rearrangement or so-called "equilibration" of silicone fluids. Base-catalyzed polymerization has been employed for the preparation of silicone rubber gum stock (polydimethylsiloxanes of high molecular weight) from low molecular polydimethylsiloxanes.[6] In particular base-catalyzed polymerization of octamethylcyclotetrasiloxane (I) has been described.[6] The strong base which has been customarily used is anhydrous potassium hydroxide[7] and reaction times up to several hours are desirable for the preparation of polymeric diorganosiloxanes.

II. Mechanism of the Rearrangement Reaction

No matter what the mechanism of the polymerization of polydimethylsiloxanes, it is apparent that the process must involve an opening and closing of silicon–oxygen bonds, that is, a reshuffling of siloxane linkages. In the absence of chain-terminating units and any thermodynamically favored molecular form, a random shuffling of siloxane linkages would be expected to lead to high molecular weight forms as the most probable forms. On the basis of this random reshuffling, there should be a distribution of molecular weights; this distribution has been observed in practice by fractionation techniques. At equilibrium, increased amounts of chain-terminating groups would be expected to yield products of lower average molecular weight. This effect also may be observed in practice.

There appear to be two distinct although related steps in the mechanism whereby a strong base such as potassium hydroxide can catalyze the polymerization of a polysiloxane: (a) the entry of the catalyst molecule into the siloxane system, and (b) the continued action of the catalyst molecule, or some part of it, in the reshuffling of siloxane linkages.

We have postulated that the first step in the base-catalyzed reaction is the coördination of the oxygen atom in the potassium hydroxide molecule to a silicon atom in a siloxane chain, and a subsequent rearrangement of the activated complex with chain cleavage. (It will be understood that, unless they are otherwise designated, the silicon atoms will also be linked to two methyl groups and to one other oxygen atom as parts of large molecules.)



$$\mathrm{Si{-}O{-}Si} + \mathrm{KOH} \longrightarrow \mathrm{Si{-}O{-}}\underset{\substack{\uparrow \\ \mathrm{KOH}}}{\mathrm{Si}} \longrightarrow \mathrm{Si{-}O{-}K} + \mathrm{H{-}O{-}Si} \qquad (1)$$

Once the potassium hydroxide has entered the siloxane chain in the form of the potassium silanolate — SiOK, it is proposed that this is the active species in causing further siloxane rearrangements. This assumption is substantiated by the fact that metal silanolates have been shown to bring about siloxane rearrangements.[8]

The silicon atom appears to be a relatively good electron acceptor. It is known that silicon can coördinate electron donor groups such as, for example, fluoride ion in the formation of the fluosilicate ion, and that certain reactions of silicon compounds do proceed through intermediate coördination complexes.[9] There are, in fact, compounds known in which silicon coördinates as many as six oxygen atoms.[10]

Now, one would expect that if coördination of the oxygen atom as an electron donor to the silicon atom were the first step in reaction,[2] increasing the efficiency of the oxygen as an electron donor should decrease the temperature at which the base becomes soluble in the siloxane and, possibly, increase the rate of solution. As evidence for this, we have observed that whereas potassium hydroxide does not dissolve appreciably in I until a temperature of about 130° has been reached, cesium hydroxide dissolves at 100° or lower. Sodium hydroxide, a weaker base than potassium hydroxide, does not dissolve at 150° and, in fact, seems to be ineffective in catalyzing the polymerization reaction at this temperature. Lithium hydroxide similarly is ineffective; it does not appear to dissolve, and it produces no apparent polymerization of I in 16 hours at 175°. Potassium oxide, in which the oxygen atom presumably is a strong electron donor, dissolves quite rapidly in the siloxane at 150° and does promote the polymerization reaction.

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[1] Presented before the Division of Physical and Inorganic Chemistry, American Chemical Society Meeting, Chicago, Ill., September, 1953.

[2] W. I. Patnode and D. F. Wilcock, THIS JOURNAL, **68**, 360 (1946).

[3] M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, *ibid.*, **68**, 667 (1946).

[4] M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Curie, *ibid.*, **68**, 2284 (1946).

[5] D. W. Scott, *ibid.*, **68**, 2294 (1946).

[6] J. F. Hyde, U. S. Patent 2,443,353, June 15, 1948.

[7] E. L. Warrick, U. S. Patent 2,634,252, April 7, 1953.

[8] J. F. Hyde, U. S. Patent 2,634,284, April 7, 1953.

[9] C. G. Swain, R. M. Esteve and R. H. Jones, THIS JOURNAL, **71**, 943 (1949).

[10] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, Oxford, 1945, p. 459, *et seq.*

We have observed that certain compounds containing strong electron donor groups other than oxygen also are capable of coördinating to, and catalyzing the polymerization of, siloxane systems. For example, potassium amide, in which the nitrogen atom is a strong electron donor, dissolved very rapidly in I at 150° and caused the formation of high molecular weight polydimethylsiloxane.

The reaction delineated by equation 1 above undoubtedly is reversible, and it should be noted that this type of reaction could be used alone to explain the reshuffling of siloxane linkages. However, we consider that it probably plays a minor role in the redistribution process, and that the amount of reversibility in this reaction actually is small, particularly at the low catalyst concentrations normally employed.

We believe the second step in the reaction to be a rapid exchange reaction. (The stars are used

$$\overset{*}{\mathrm{Si}}\text{–O–}\overset{*}{\mathrm{Si}} + \mathrm{Si}\text{–O–K} \longrightarrow \overset{*}{\mathrm{Si}}\text{–O–Si} + \overset{*}{\mathrm{Si}}\text{–O–K} \quad (2)$$

here to differentiate individual silicon atoms, and it should be remembered that these units are parts of larger molecules.) This reaction, like the initial reaction step, also must depend on the formation of intermediate coördination complexes, in this case through the action of the oxygen atom in the Si–O–K as an electron donor, and also will be influenced by the electropositivity of the alkali metal component. This reaction is, of course, reversible, but with a large concentration of siloxane and a small concentration of catalyst, the probability that the particular molecular units designated as $\overset{*}{\mathrm{Si}}\text{–O–Si}$ and $\overset{*}{\mathrm{Si}}\text{–O–K}$ would react again would be small in comparison to the probability that the $\overset{*}{\mathrm{Si}}\text{–O–K}$ unit would react with a different siloxane linkage. From the present study it is not possible to determine whether reaction 1 or reaction 2 is the rate-determining step, although it is expected that the choice may vary depending on the particular siloxane-catalyst combination employed.

The authors have observed qualitatively that the polymerization of I is brought about at the same rate by potassium amide and potassium hydroxide at 150°. This might be expected, since in a large excess of the siloxane, both these materials should yield the same active intermediate, *i.e.*, –SiOK. On the other hand, if potassium is replaced by a more electropositive metal, such as cesium, the polymerization reaction not only proceeds much more rapidly, but will proceed at a much lower temperature. It appears thus that the enhanced ability of the oxygen as an electron donor is maintained in the Si–O–Cs groups throughout the course of the polymerization. Conductivity experiments (*vide infra*) indicate that the Si–O–Cs unit is not appreciably ionized in the siloxane medium at 150°. Thus it has been established the order of reactivity of bases toward I at elevated temperatures is CsOH > RbOH > KOH > NaOH, or in other words the reactivity is related directly to the size of the cation.

A further consequence of the proposed mechanism is that the molecular weight of the polymer should depend on the nature of the catalyst. If, for example, the hydroxy group that becomes attached to one end of a siloxane chain during the first step of the process is relatively unreactive, it will act more or less as a temporary chain-terminating unit; this will tend to keep the average molecular weight of the polymer lower than that which would be expected in the absence of chain-terminating groups. However, hydroxyl groups can be lost by condensation reactions between Si–O–H units. Thus, for polymerizations conducted in open systems and over long periods of time, it is probable that most of the hydroxyl groups become lost in this fashion, and so are ineffective as permanent chain stoppers; high molecular weight gums eventually are obtained. On the other hand, if large and presumably inactive groups such as the methoxy group are present (polymerization with potassium methoxide, see Experimental section), these groups act as permanent chain-terminators, and soft gums of low molecular weight are obtained. These soft gums do not become firm on extended heating, so the effect is not one dependent on the rate of polymerization.

III. Rearrangement Reactions in Alcoholic Media

We observed that the base-catalyzed siloxane rearrangement process could be studied at room temperature by polymerizing I with various bases in a medium of anhydrous methanol or ethanol. The polydimethylsiloxanes of low molecular weight including I are soluble in methanol over a wide range of concentrations. The polydimethylsiloxanes of high molecular weight, however, are not appreciably soluble in methanol; and if a solution of I in methanol is caused to polymerize, the higher molecular weight siloxanes separate as a distinct phase. Although we made no attempt to determine the relation of siloxane molecular weight to solubility in methanol, the separation of the higher molecular weight products as a new phase was useful in comparing the relative effectiveness of different bases in promoting the polymerization of I. It will be noted that this technique, in which the base in alcohol solution was added to the alcohol solution of I, eliminated the uncertainty of any inadequate dispersal of a difficultly soluble, powdered solid in hot siloxane. It is assumed, however, that the coördination of the alkali metal hydroxide, or methoxide, to the siloxane still occurred as the preliminary step in the arrangement and polymerization reaction.

We found that the time required for the appearance of the second phase in the alcoholic polymerization reaction was dependent on both the concentration of I and the concentration of the base in the methanol solution, as well as on the nature of the base. Under certain conditions, it was possible to obtain systems which exhibited turbidity almost immediately on addition of the alcoholic base, and the appearance within a few minutes of a distinct second phase which gradually increased in volume as the polymerization reaction proceeded. Although it was recognized that the new phase in such cases was not entirely polymeric product, being swollen with I and methanol, it was indeed surprising that the polymerization reaction proceeded so rapidly at room temperature. The base concentrations used were too small for any "salting-out" effect, as indicated by the fact that homogeneous solutions were obtained initially.

By setting up a series of similar systems with different bases, it was possible to make some fairly quantitative comparisons of the relative effectiveness of different bases in promoting the polymerization reaction (see Experimental). As we expected, both cesium and rubidium hydroxides caused a more rapid polymerization of I than potassium hydroxide. Tetramethylammonium methoxide was almost as effective as cesium hydroxide. This was expected, however, since quaternary amine bases are observed to be quite effective in catalyzing the polymerization of organosiloxanes at elevated temperatures.[6]

It should be recognized that these polymerization experiments in alcohol are not strictly comparable with the polymerization of I with base at elevated temperatures. For one thing, the polymeric siloxanes obtained, although of considerably higher molecular weight than I, would be chain-terminated with methoxy groups for the most part. Their average molecular weight would depend on the relative concentration of alcohol and siloxane, but in any case would be very low relative to the average molecular weight of a firm silicone gum. The experiments do, however, correlate base strength with catalytic activity; in this respect, the observations agree well with those previously made on the polymerization of pure I.

IV. Conductivity Measurements

Conductivity measurements were first made to determine whether the active silanolate intermediate (Si–O–M where M is Cs, Rb or K) was appreciably ionized in the siloxane medium during the rearrangement reaction. A number of experiments made with the most sensitive equipment available, indicated clearly that any ionization was so small as to be negligible. Very small and transitory rises in conductivity were observed immediately following the solution of the base in the siloxane at the elevated temperature, but this effect was found to be caused by the small amount of water originally present in the hydroxide, or that formed by silanol condensation.

After the unusually rapid polymerization of I in absolute methanol had been observed, a few conductivity measurements were made on this system to obtain, if possible, additional information on the rate of the reaction. This sort of information was considered to be useful, since little is known about the effect of traces of catalytic impurities on the physical and chemical behavior of silicone materials. These experiments corroborated the observations made visually; the reaction of I with rubidium hydroxide, for example, was found to occur immediately on mixing, and to proceed quite rapidly. Of particular interest was the observation that linkages between trimethylsiloxane units were not affected by base in alcohol at room temperature, although such linkages are attacked at 150°. This behavior probably is indicative of a steric effect acting to inhibit the coördination reaction.

V. Experimental

A. Polymerization of Polyorganosiloxanes. Potassium Hydroxide Polymerizations.—Powdered potassium hydroxide (0.05% by weight) added to I at 150° dissolved slowly and, over the course of 45 minutes, catalyzed the polymerization of the siloxane to a soft gum. The time required to reach approximately the same gum stage at 175° was about 10 minutes.

Cesium Hydroxide Polymerizations.—In a typical experiment, 0.03% by weight of powdered CsOH (Fairmont Chemical Co.) was added to 220 g. of I at 100°. Within about five minutes, I was polymerized to a stiff gum. In fact, the increase in viscosity was so rapid that the gum state was reached before all of the hydroxide could be stirred into solution.

Rubidium Hydroxide Polymerizations.—An amount of rubidium hydroxide (Kahlbaum) equal to 0.05% by weight added to I at 150° caused the polymerization of I within 15 minutes to a stiff gum. It was noted that the rate at which gum was formed was roughly about intermediate between that of the very rapid CsOH polymerization and the slower KOH polymerization.

Effect of Lithium and Sodium Hydroxides.—Neither of these materials appeared to catalyze the polymerization of I within 16 hours at the reflux temperature of 175°. It is reported, however, that these materials do cause some polymerization of I under more drastic conditions.[11]

Potassium Methoxide Polymerization.—Potassium methoxide was prepared by dissolving potassium in anhydrous methanol. The solution was evaporated to dryness *in vacuo*. A 0.1% solution of $KOCH_3$ in I (the compound is soluble in I at 70°) at the reflux temperature of 175° caused the polymerization, within about 10 minutes, of I to a very soft gum. This gum showed no increase in viscosity on extended heating, indicating that the methoxy groups probably were acting as permanent chain-terminators and thus depressing the average molecular weight.

Sodium Methoxide Polymerization.—Eimer and Amend reagent grade sodium methoxide (0.16%) in I produced, upon refluxing for about two hours at 175°, a very soft and semi-fluid gum. Prolonged refluxing caused no apparent increase in viscosity. This experiment was considered interesting, however, as an example of the effect of solubility on the polymerization reaction; sodium hydroxide did not react at all under these conditions.

Potassium Oxide Polymerization.—Potassium oxide was prepared by burning potassium metal in air in a nickel crucible. The material obtained was colored green, owing to the presence of nickel, and undoubtedly contained higher oxides of potassium as well as K_2O. An amount of this material equivalent to 0.02% dissolved rapidly in I at 175° and produced a hard gum in about five minutes at this temperature.

Potassium Amide Polymerization.—Potassium amide was prepared by heating potassium metal in ammonia gas at 300°, and allowing the amide to cool in ammonia. About 0.17 g. of KNH_2 in 60 g. of I produced a gum in two to three minutes at 175°. It was observed that the amide dissolved very rapidly in the hot siloxane.

B. Polymerization of Tetramer in Alcohol.—Polymerizations of I in anhydrous methanol were made at a number of different concentrations and with different bases. Although it was possible to obtain systems which exhibited evidence of polymerization within a very few minutes after adding the base to the siloxane–alcohol mixture, we used slower acting systems to measure comparative rates with different bases. The experiment below is typical:

Four solutions were prepared, each of which contained 13 cc. of I diluted to 25 cc. with methanol, and containing a small amount of brom thymol blue (soluble in methanol but not in I). Each solution also contained 5×10^{-4} mole of base, added in alcoholic solution. The bases were (a) CsOH, (b) RbOH, (c) KOH, (d) $(CH_3)_4N–O–CH_3$. Elapsed time movies were taken of these four solutions contained in stoppered 25-cc. graduates; one frame was taken per minute. In 15 hours a meniscus was noticed with CsOH, RbOH and the quaternary base. This meniscus occurred at the 19-cc. mark and apparently was due to the formation of a siloxane phase containing a large quantity of dissolved methanol; the dye was distributed between the two phases.

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(11) J. F. Hyde, U. S. Patent 2,490,357, December 6, 1949.

At 22 hours, a bottom phase free of dye appeared in the RbOH solution; the volume of this phase increased from 6 cc. at 22.75 hours to 14 cc. in 23 hours. The same volume of phase free of dye formed in the CsOH solution in 35 hours and a similar volume of the dye-free phase formed in the quaternary base solution in 36 hours. In the KOH solution, a meniscus was barely visible in 43 hours and in 52 hours at the conclusion of the experiment, no dye-free phase had formed. We can offer no good explanation why RbOH caused a more rapid polymerization than did CsOH in the methanol solution, and this same effect was observed in other experiments in methanol.

One large-scale experiment was carried out. A mixture of 260 cc. of I, 140 cc. of methanol and 20 cc. of 0.1 N CsOH was placed in a stoppered flask and allowed to stand six days at room temperature. The silicone layer was then separated, washed three times with water and allowed to stand over Amberlite Resin 100H. The neutral product was washed again with water and dried over anhydrous sodium carbonate. A 200-cc. sample was subjected to distillation. Approximately 25% of I was recovered unchanged; 5% of the sample boiled from 100–120° at 47 mm., 27% from 100 to 150° at 21 mm., 8% from 120 to 150° at 1 mm., and the remaining 35% consisted of material boiling at a temperature higher than 160° at 1 mm. It is obvious that a considerable amount of high molecular weight material was formed in the room temperature reaction with cesium hydroxide.

C. Conductivity Measurements. Measurements in Octamethylcyclotetrasiloxane.—A small beaker of I was set on a hot-plate and equipped with a pair of platinum electrodes. The resistance of the liquid was measured continuously with a General Electric photoelectric recorder; the circuit constants were such that a full-scale deflection was equivalent to 100 megohms resistance, and conductivities as small as those corresponding to resistances of 2×10^{12} ohms would clearly be indicated. The applied measuring voltage was *ca.* 150 v. d.c. The resistance of I remained practically at infinity as the liquid was heated to *ca.* 100°. At this point, a small amount of CsOH (0.1%) was added to the I. No immediate change in the resistance of the mixture was noted, but after several minutes, as the hydroxide dissolved and the temperature rose to *ca.* 120°, a very slight increase in conductivity was observed, then a rapid decline back to essentially infinite resistance as I polymerized to a stiff gum. The lowest resistances measured in the process still were thousands of megohms.

Since there was some doubt about the possibility of conduction in such a stiff gum, experiments also were made in a medium of hexaethyldisiloxane, using the photoelectric recorder. When *ca.* 0.50% of powdered potassium hydroxide was added to 20 ml. of hexaethyldisiloxane at 130° (in test-tube fitted with Pt electrodes and immersed in constant temperature-bath of silicone oil), a small increase in conductivity was observed immediately. The conductivity increased slowly for about ten minutes to a maximum of *ca.* 1×10^{-10} ohms, then decreased over an approximately equivalent time to almost infinite resistance. In a similar experiment, the addition of *ca.* 0.5% of CsOH to hexaethyldisiloxane caused a very sharp increase in conductivity; the initial rate of change of conductivity with time was approximately 20 times as great as that with KOH. The decline in conductivity was at about the same rate as with KOH, however. We observed that the addition of one tiny drop of water to the system either with KOH or with CsOH, after the resistance had assumed its original low value, caused a sharp rise in the conductivity followed by a slow decay to essentially zero conductivity as the water distilled out of the hot siloxane.

The very low level of conductivity of the solutions of KOH or CsOH in I or hexaethyldisiloxane at temperatures of 120–150° certainly indicates that the intermediate metal silanolate complexes are not appreciably ionized. A 0.5% solution of either of these hydroxides in anhydrous methanol, for example, exhibits a relatively high conductivity.

It should be pointed out that both KOH and CsOH normally are not completely anhydrous materials, thus some water is present before the solubilizing reaction can begin. However, the amount of water formed by reaction of the hydroxide and condensation of the silanols thus formed is considerably in excess of the amount of water normally present in the hydroxide. Also, the conductivity does not increase appreciably until the hydroxide begins to dissolve in the hot siloxane. This argument does not affect the conclusion, previously drawn, that the metal silanolate complex is essentially un-ionized in the siloxane medium.

Measurements in Alcohol–Siloxane Systems.—The voltage source for these resistance measurements was an audio-frequency generator with adjustable output. The signal from the generator was applied to the test cell (Pt electrodes) through a suitable resistance (20–200 ohms depending on the conductivity of the liquid in the cell). The voltage developed across this resistance then was rectified with a 1N34 crystal and measured on a photoelectric recorder (1 microamp. sensitivity, but sensitivity was adjusted with resistors to fit experiment). The frequency used was usually 2 kc. or 20 kc. and did not seem to be at all critical; a.c. was used only to avoid the polarization effects that were noticed when measurements were made with d.c. in systems of such relatively high conductivity. No attempts were made to measure absolute values of resistance or conductivity, only the changes in these quantities.

All the solutions of salts or base in alcohol were made several days prior to the measurements since it was observed that the resistance of such solutions changed somewhat during the first few hours after mixing. Solutions in absolute ethanol were used for the most part since such solutions exhibit a lower change in specific resistivity with viscosity than do methanol solutions; the results with methanol solutions were approximately the same, however.

1.—10 ml. of 0.5% solution of RbOH in EtOH was placed in cell, input adjusted to give *ca.* half-scale reading on recorder and apparatus allowed to run for a few minutes until recorder reading became constant. Then 1 ml. of I was added. An immediate drop in conductivity to about 50% of the original value occurred due to dilution and increase in solution viscosity, then a slow decline in conductivity to a lower and constant value, about $^1/_6$ of original value, in *ca.* $^3/_4$ hr. The voltage then was raised to bring reading back up-scale on the recorder. The addition of a second 1 ml. amount of I again produced a very rapid decline in conductivity due to dilution and viscosity increase, but no slow decline following this drop. This indicated that the first ml. of I had reacted with all the available RbOH in the system.

2.—This experiment was conducted under the same conditions as experiment 1 except that a solution of CsCl in EtOH (*ca.* 0.25%) was used instead of RbOH. Addition of I produced immediate drop to *ca.* 50% conductivity due to dilution and viscosity increase, but then recorder remained constant at this value. Thus, there appears to be no reaction of I with CsCl in EtOH.

3.—Experiments 1 and 2 were repeated with 8 drops of water added to the ethanol solutions before addition of I. In the CsCl experiment no differences were noted. With RbOH, however, the water seemed to accelerate the reaction of the siloxane with the base; the slow decline to *ca.* one-sixth of the original conductivity was complete in 20 minutes. The system showed the same conductivity after standing 24 hours as it did after 20 minutes.

4.—Experiment similar to 1. RbOH solution in ethanol in test cell (10 ml.). Then 1 ml. of hexaethyldisiloxane added. Immediate drop in conductivity to 50% value noted, but no further decline. This indicated that this siloxane did not react with RbOH at room temperature in ethanol. To show that RbOH still was active, 1 ml. of I was added to the solution. This produced the same sharp drop and subsequent slow decline to much lower value over an extended period as was observed with I in experiment 1.

5.—Experiment similar to 4, but with hexamethyldisiloxane. Again no reaction was observed but reaction with I added later did occur. From the evidence observed, it appears that trimethylsiloxane units do not react, at least at any appreciable rate, with RbOH in ethanol at room temperature. Thus a $(CH_3)_2SiO$– unit is more reactive under these conditions than a $(CH_3)_3SiO_{1/2}$– unit.

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